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The i.r. spectra of several rare-earth formates

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Abstract—The i.r. spectra of some rare-earth formates are recorded in the range 4000–40 cm^{-1}. The following compounds were studied: $Ce(HCO_2)_3$, $Pr(HCO_2)_3$, $Nd(HCO_2)_3$, $Sm(HCO_2)_3$, $Eu(HCO_2)_3$ and $Gd(HCO_2)_3$. Some compounds were also studied upon deuteration and at lowered temperature. Nearly all bands could be assigned and the expected factor group splitting was observed. A shift to higher frequencies was observed with increasing atomic number.

INTRODUCTION

FERRARO and BECKER [1] have studied $La(HCO_2)_3$, $La(DCO_2)_3$ and $Nd(HCO_2)_3$; they gave an assignment in terms of metaloxygen stretching for some far i.r. frequencies. We could assign nearly all bands according to the factor group analysis in the case of gadolinium formate, for which compound the structure has been revealed by PABST [2]. MAYER [3] has concluded from his X-ray studies, that cerium-, praseodymium-, neodymium- and samariumformate are isostructural with gadolinium formate. The striking resemblance of all recorded spectra greatly supports Mayers conclusion and indicates that europium formate also belongs in this series.

EXPERIMENTAL

All compounds were prepared by dissolving the oxydes (FLUKA, puriss.) in diluted nitric acid, precipitating the carbonates by adding sodiumcarbonate (BDH, Analar). The precipitates were washed out with deionized water until a pH of 7–8 was obtained. These washed out precipitates were dissolved in formic acid (BDH, Analar). When the precipitated carbonates were still wet, the formed formates stayed dissolved and could be obtained by slow evaporation. Dried, the carbonates gave a solid state reaction without dissolution of the formate. Only gadolinium formate is soluble in water. We used both methods without distinction. Checking upon one compound revealed that there is no difference in the spectra, indicating, that the structure of the compounds, —made by the two methods— is identical.
The spectra were recorded as potassiumbromide discs and polyethylene discs on a Hitachi EPI G3 i.r. and a Beckman-RIIC FS 720 Fourier far i.r. spectrophotometer. The low temperature spectra were recorded using a home-made liquid nitrogen cryostat, which could attain at least −150° C.

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RESULTS

The crystal structure of gadolinium formate has been studied by PABST [2]. It has a rhombohedral lattice $C^5_{3v}(R3m)$ spacegroup. Table 1 contains the results of the factorgroup analysis. Table 2

Table 1. Factor group splitting for gadolinium formate with spacegroup $C_{3v}{}^5$

C^5_{3v}	N_{tot}	N_{ac}	N_{tr}	N_{rot}	$N_{int}^{formate}$	activity
A_1	9	1	2	1	5	R, IR
A_2	4	0	1	2	1	
E	13	1	3	3	6	R, IR

Table 2. Wavenumbers and assignments for gadoliniumformate

Description	Sym.spec.	$Gd(HCO_2)_3$	$Gd(DCO_2)_3$	Intensity
ν_{C-H} or ν_{C-D}	E, A_1	2915	2220	w
$\nu_{C-O_{asym}}$	E	1600	1583	str, br
	A_1	1575	1546	sh
δ_{O-C-H} or δ_{O-C-H}	E, A_1	1413	1059	str, shp
$\nu_{C-O_{sym}}$	E	1368	1340	str, shp
	A_1	1360	1328	str, shp
$\pi_{H(CO_2)}$ or $\pi_{D(CO_2)}$	E	1090	917	v.w.
δ_{O-C-O}	E	789	780	str, shp
	A_1	780		sh
T_x, T_y, T_z	E, A_1	306	307	br
			298	br
		266	265	br
		236	233	br
R_x	A_1	203	198	shp
	E	180	178	br
R_y	E	168	155	br
R_z	E	141	136	shp

w=weak. str=strong; br=broad; shp=sharp; sh=band is accompanied by a shoulder; v=very

Overtone and combination bands.

$Gd(HCO_2)_3$	$Gd(DCO_2)_3$	assignment
	3545	2220 + 1328
	2987	2220 + 780
	2913	2 × 1583
2840	2853	1546 + 1340
	2633	2 × 1328
	2375	1328 + 1059
	2160	
	2090	1328 + 780
1436 (str)	1426 (w)	
	1358	

Table 3. Wavenumbers for the rare-earth formates

La		Ce		Pr	Nd		Eu	Sm	Gd		
HCO_2	DCO_2	HCO_2	DCO_2						HCO_2	DCO_2	
										3545	
										2987	
* 2856[a]	2208[a]	2905	2195	2905	2915		2918	2918	2915	2220	w
										2913	
			2830	2840			2845	2845	2840	2853	
		2750		2763							
		2675		2685						2633	
										2375	
										2160	
										2090	
* 1605[a]	1585[a]	1596	1586	1595	1594		1598	1602	1600	1583	br,str
* 1580[a]	1550[a]	1575	1544	1582	1577		1578	1578	1575	1546	sh or shp
1428[a]		1425	1415	1429	1430		1432	1432	1436	1426	shp,str
* 1405[a]	1056[a]	1404	1052	1409	1408		1410	1410	1413	1059	shp,str
					1382		1383		1380	1358	v.w.
* 1358[a]	1334[a]	1355	332	1362	1365		1365	1366	1368	1340	shp,str
*	1328		322	1357	1359		1357	1358	1360	1328	sh or shp
*		1086	915	1091	1100			1093	1090	917	v.w.
* 779[a]	770[a]	779	775	786	786		786	786	789	780	shp,m
*				778	780			778	780		sh or shp
*		306								307	shp
*	280[a]	283		286	292	282[a]	303	300	306	298	br,str
* 262[a]		250		253	253	240[a]	265	261	266	265	br,str
* 238		228		233	228		240	236	236	233	br,str
*		186			198		197	194	203	198	sh or shp
* 167[a]		174		179	178	183[a]	185	178	180	178	br,str
* 150[a]		155		158	161	163[a]	169	166	168	155	m,shp
* 121[a]		124		127	132	133[a]	139	137-	141	136	m,shp

a) data from Ferraro and Becker [1]

* = fundamental

Table 4. Calculations of the moments of inertia for the formategroup in $Gd(HCO_2)_3$ and $Gd(DCO_2)_3$. Data for carbon and oxygen are taken from PABST [2]. The hydrogen atom is supposed to have a carbon—hydrogen distance of 1.09 Å and to make equal angles with the two carbon—oxygen bonds

MOMENTS OF INERTIA (Atomic units)				CARTESIAN COORDINATES			
	I_x	I_y	I_z		X	Y	Z
HCO_2	47.217	6.000	41.218	H	2.3390	0.0	7.8855
DCO_2	49.504	8.284	41.220	C	2.5307	0.0	6.8126
Ratio	0.954	0.724	1.000	O	1.5063	0.0	5.9627
203/198	0.9753			O'	3.7357	0.0	6.3877
180/178	0.9888						
168/155		0.9226					
141/136			0.9645				

contains the observed frequencies and the assignments for gadolinium formate. In Table 3 are listed the data for all the studied formates, clearly indicating the resemblance of the spectra as well as the shift in frequency with increasing atomic number.

DISCUSSION

The assignment for the internal formate wavenumbers is based on the assignment for sodium formate [4], lanthanum formate [1] and formaldehyde [5], assuming the E-mode higher in wavenumbers than the A_1-mode; this is based on the "molecular" argument, that asymmetrical vibrations are higher in wavenumbers than the symmetrical ones. There is a striking feature in the 1400–1450 cm^{-1} region.

The two bands in this region are assigned by Ferraro and Becker as a splitting of the in plane rocking (δ_{C-H}). Their deuteration study showed the shifted band to be single, thus the splitting of the rocking being undetectable. Our deuteration study showed the same shift for the lower of the two bands and a remaining very weak band somewhat between the two bands from $Gd(CHO_2)_3$. These bands are temperature independent; we think therefore that this band is a combination band, which owing to Fermi resonance has grown in intensity.

Deuteration studies are very helpful in the assignment of the librational modes. In Table 4 the results are listed of calculations of the moments of inertia for the formategroup in gadolinium formate. Studies on sodium formate [6] with C_2 site symmetry for the formate ion indicate $\tilde{\nu}_{R_x} > \tilde{\nu}_{R_y} > \tilde{\nu}_{R_z}$ more clearly than in the case gadolinium formate.

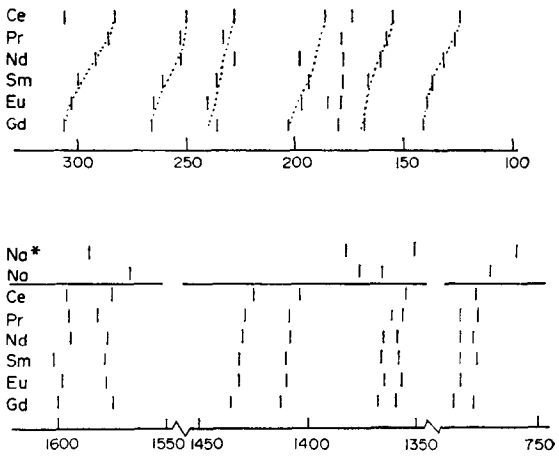

Fig. 1. Wavenumbers for the rare earth formates Ce, Pr, Nd, Sm, and Gd. The shift to higher wavenumbers and the increase of crystal field splitting in the series cerium to gadolinium. For comparison some of the wavenumbers of sodiumformate are given (Na: solid, Na*: aqueous solution).

In gadolinium formate the formate ion has C_s symmetry, thus R_x and R_z are in the same symmetry species and can mix.

The translational modes are more difficult to assign; the spectra show 3 broad bands with in some spectra an additional sharp band. Deuteration gives only a very small calculated shift, which cannot be seen in the spectra, because of the inaccuracy in the wave number of the broad bands.

We think therefore that the three broad bands in the region 200–300 cm^{-1} are the three species translational modes, but we have no information to distinguish them between T_x, T_y and T_z. The additional sharp bands must then be assigned to the A_1 species.

Assuming an identical structure with small changes in the cell dimensions it is remarkable to see the shift to higher frequencies and the increase of the crystal field splitting of nearly all vibrations with increasing atomic number, as shown in Fig. 1.

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